

Oxidation of Hydrogen Sulfide to Elemental Sulfur from Coal-Derived Fuel Gases

Todd H. Gardner
Dushyant Shekhawat
David A. Berry

U. S. Department of Energy
National Energy Technology Laboratory
P. O. Box 880
3610 Collins Ferry Road
Morgantown, WV 26507

Abstract

Vision 21 is the U. S. Department of Energy's initiative to deploy high efficiency, ultra-clean co-production coal conversion power plants in the twenty-first century. These plants will consist of power and co-production modules, which are integrated to meet specific power and chemical markets. Sweetening of the fuel gases derived from these plants, down to the parts-per-billion level, is necessary since many co-production modules contain catalysts that are sulfur intolerant.

The selective catalytic oxidation of hydrogen sulfide (SCOHS) technology currently being sponsored at NETL integrates gas conditioning, e.g. amine absorbers, and gas treating, e.g. Claus plants, systems into a single overall step. The result is a simpler, lower cost system for attaining a sulfur free coal-derived fuel gas. In this process, the microporous catalyst catalyzes the reaction: $\text{H}_2\text{S} + 1/2\text{O}_2 \Rightarrow 1/n\text{S}_n + \text{H}_2\text{O}$ at temperatures between 100 and 150°C. The elemental sulfur produced is deposited within the pores of the catalyst acting as a medium for storage of the sulfur product. Over time the catalyst becomes saturated with sulfur and must be thermally regenerated. Regeneration occurs at 350°C in nitrogen, which drives off the elemental sulfur as vapor and restores catalyst activity. Current research is focused on optimization and testing of new catalyst systems and developing engineering design parameters for scale-up and modeling of this novel process.

Introduction

The development of low cost, highly efficient, desulfurization technology with integrated sulfur recovery remains a principle barrier issue for Vision 21 integrated gasification combined cycle (IGCC) power generation plants. In this plan, the U. S. Department of Energy will construct ultra-clean, modular, co-production IGCC power plants each with chemical products tailored to meet the demands of specific regional markets. The catalysts employed in these co-production modules, for example water-gas-shift and Fischer-Tropsch catalysts, are readily poisoned by hydrogen sulfide (H_2S), a sulfur contaminant, present in the coal-derived fuel gases. To prevent poisoning of these catalysts, the removal of H_2S down to the parts-per-billion level is necessary.

Historically, research into the purification of coal-derived fuel gases has focused on dry technologies that offer the prospect of higher combined cycle efficiencies as well as improved thermal integration with co-production modules. Primarily, these concepts rely on a highly selective process separation step to remove low concentrations of H_2S present in the fuel gases and produce a concentrated stream of sulfur bearing effluent. This effluent must then undergo further processing to be converted to its final form, usually elemental sulfur. Ultimately, desulfurization of coal-derived fuel gases may cost as much as 15% of the total fixed capital investment (Chen *et al.*, 1992). It is, therefore, desirable to develop new technology that can accomplish H_2S separation and direct conversion to elemental sulfur more efficiently and with a lower initial fixed capital investment.

The most direct path for sulfur production from hydrogen sulfide is via the reaction:



Thermodynamically, reaction (1) has the potential to remove H_2S to the parts-per-billion level below 250°C. This reaction has already found application in commercial Claus tail gas cleanup technologies (Lagas *et al.*, 1988) and application of this technology continues to be the subject of ongoing research in natural gases wellhead desulfurization (Kensell and Leppin, 1995; Dalai and Tollefson, 1998). However, relatively little work applying reaction (1) to the desulfurization of coal-derived fuel gases has been reported in the literature. In contrast to tail gases and natural gas, coal-derived fuel gases contain significant quantities of carbon monoxide (CO) that can react with the sulfur that is produced to form carbonyl sulfide (COS). Meyer *et al.* (1997) has discussed an activated carbon sorbent injection system where air that is co-injected with an activated carbon catalyst selectively oxidizes the hydrogen sulfide present in a coal-derived fuel gas to elemental sulfur. Their results indicate that sulfur removal to very low levels was possible below 200°C. Above 200°C the formation of COS became problematic. Interestingly, Meyer *et al.* (1997) demonstrated that as the level of oxygen (O_2) partial pressure increased, COS levels decreased. This was probably due to the fact that it was CO adsorbed on the surface of the catalyst that was reacting with sulfur vapor to form COS.

Our investigation of this technology determined that the temperature range between 100 and 175°C would be desirable to explore. Under these conditions the

elemental sulfur produced via reaction (1) would be retained within the pores of the catalyst. Operationally this would ensure that undesirable side reactions could be minimized. This approach is known as the integrated reaction and separation approach. And under the conditions studied here, the elemental sulfur product is retained as a condensed phase within the pores resulting in a slow deactivation of the catalyst through active site occlusion (Dalai and Tollefson, 1998). Thermal regeneration in nitrogen may then be employed to recover the elemental sulfur as product from the pores of the catalyst.

Objective

The objective of the present work is to report on the development of a simple, dry, direct path technology that desulfurizes coal-derived fuel gases with fewer overall steps, less energy and a lower initial capital investment than the best available technology today. In this investigation, the ability of a carbon-based catalyst system was assessed for its ability to selectively oxidize the H_2S contaminant present in coal-derived fuel gases directly to elemental sulfur. The catalyst was tested at relatively moderate space velocities of $2,500 \text{ hr}^{-1}$ (STP) while undergoing catalytic reaction accompanied by capillary condensation of the sulfur product within its pores. IGCC Integratability with a preliminary cost analysis, using the Tampa Electric Company (TECO) as a baseline, was conducted to demonstrate the synergism with commercially available Texaco O_2 -blown and Destec gasification technology.

Results

Experimental Apparatus. The experimental apparatus used to conduct this series of experiments was a laboratory scale, quartz fixed bed reactor 1.16 m long by 10.5×10^{-3} m in internal diameter. Tightly packed quartz wool was used as a distributor to support the catalyst. The reactor was vertically positioned in a Lindburg single zone furnace (model No. 56447) in the down flow mode. Reaction temperature was monitored by a K-type thermocouple located externally at the center of the catalyst bed. Swagelok PFA fittings were used to seal the reactor ends with 1/8" teflon tubing used as a gas sampling line. Temperature control for the reactor was achieved using a Honeywell controller set for constant heat flux output. The coal-derived fuel gases were simulated by carefully metering and manifolding individual bottled gases supplied by Matheson Gas Products. Individual gas flow rates were controlled using MKS 1980 thermal mass flow controllers coupled with an MKS model 248C power supply.

Exit gases including H_2S , COS, CS_2 and SO_2 were analyzed using gas chromatography. H_2S was analyzed using a glass column 1/8" x 6' packed with (40/60 mesh) Carbopack BHT 100. The column was used in Perkin Elmer Sigma 300 gas chromatograph equipped with Flame Photometric Detector (FPD). SO_2 was analyzed using a teflon column 1/8" x 8' packed with Chromosil 310. The column was used in Perkin Elmer 8500 gas chromatograph equipped with a FPD. COS and CS_2 were analyzed using a teflon column 1/8" x 8' packed with Chromosil 310. The column was

used in Perkin Elmer AutoSystem gas chromatograph equipped with a FPD. Detection limits were determined to be 0.1, 1.0 and 5.0 ppmv for H₂S, COS and SO₂, respectively.

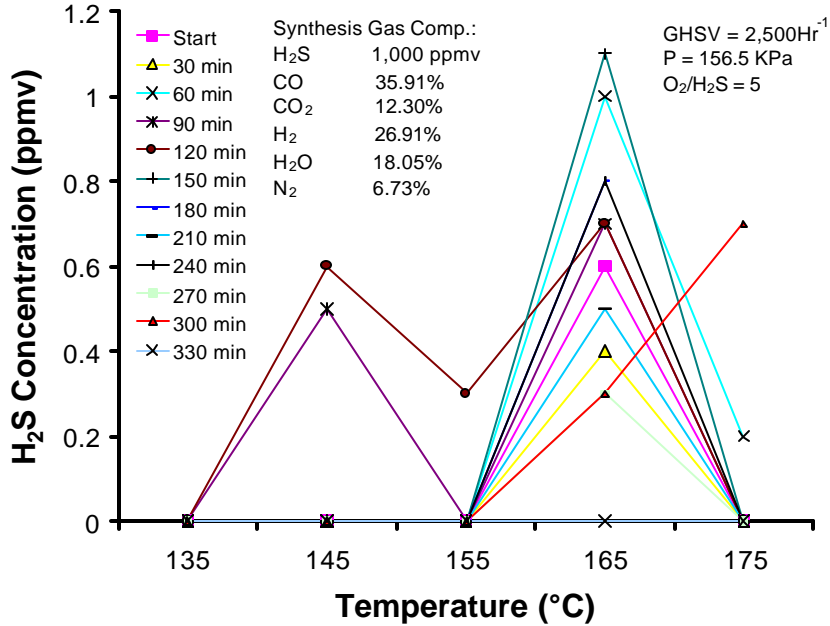


Figure 1. H₂S exit concentrations.

Experimental Results. A series of isothermal experiments, each timed to last exactly 5-1/2 hours, were conducted to assess the ability for a carbon-based catalyst to act as both a catalyst and a sulfur retaining sorbent. Each timed run was conducted at a different temperature: 135, 145, 155, 165 and 175°C. Figure 1 illustrates the ability for this catalyst to remove sulfur levels in a simulated Texaco O₂-blown gasifier gas laden with 1,000 ppmv H₂S. For this series of experiments, H₂S levels were consistently removed down to levels below 1.2 ppmv. The experiments were conducted at a GHSV of 2,500 hr⁻¹ and with an O₂/H₂S ratio of 5:1. The addition of excess oxygen was necessary to minimize the side reaction between CO and sulfur vapor to form COS.

Figure 2 illustrates that elemental sulfur tapped within the pores of the catalyst may be over oxidized to SO₂ via the reaction:



For this carbon-based catalyst, SO₂ formation was not observed below 155°C. Therefore, utilization of this technology, using this catalyst, would be restricted to a maximum operation temperature of 155°C.

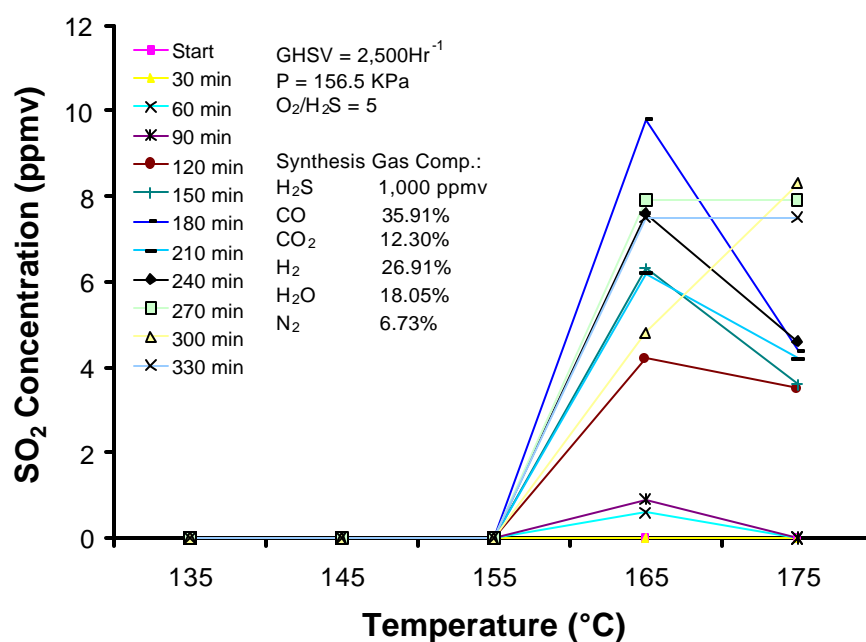


Figure 2. SO₂ exit concentrations.

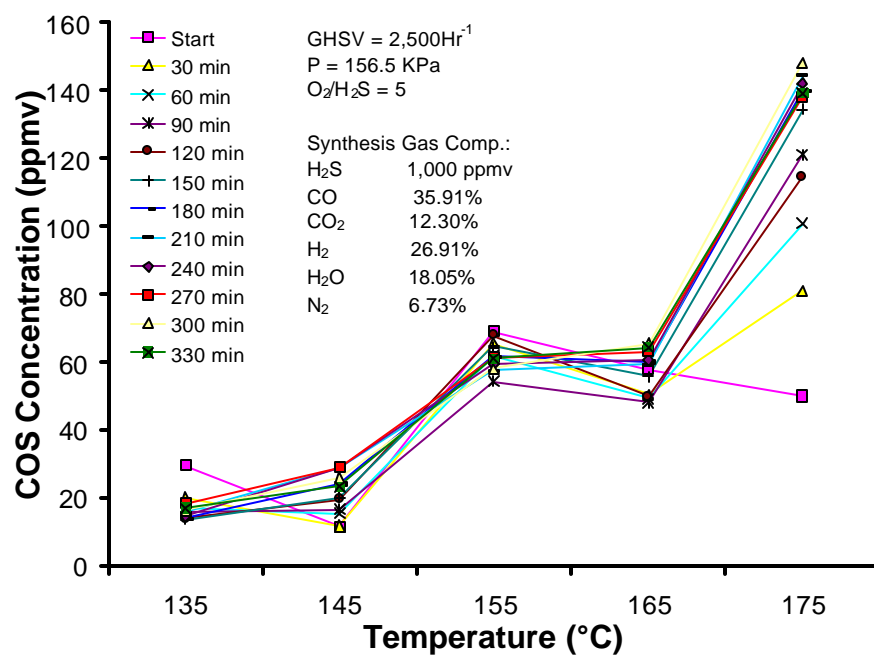


Figure 3. COS exit concentrations.

Figure 3 illustrates that CO may readily react with the elemental sulfur product to form COS via the reaction:



The strong functionality of COS formation with temperature is indicative of sulfur vapor reacting with the CO. As reaction time on stream increases and the sulfur loading of the catalyst increases, the micropores fill first. As mentioned earlier, the 5:1 ratio of O₂/H₂S was necessary to mitigate side reaction (3) from occurring. The carbon-based catalyst tested here possesses a greater affinity for O₂ over CO resulting in a displacement of CO* on the surface. This, in turn, results in lower COS levels. To maintain COS levels below 20 ppmv, an operational temperature below 145°C must be maintained.

Figure 4 is an electron dispersion spectroscopic (EDS) analysis of the cross-section of a carbon-based catalyst pellet that was exposed to a 1,000 ppmv H₂S laden simulated Texaco O₂-blown gasifier gas for 5-1/2 hours. The sulfur profile, indicated in red, within the pellet is that of a sharp interface. This indicates that the reaction is diffusion controlled, with the reaction taking place significantly faster than reactant diffusion and adsorption onto an active site.

Details of a highly preliminary systems analysis of the SCOHS process are given in Table 1 (Rutkowski *et al.*, 2001). As a baseline case the IGCC plant located at Tampa, Florida (TECO) was utilized to develop a normalized comparison between cold gas cleanup and SCOHS. These preliminary results indicate that approximately a 7% reduction in the COE (\$/MWh) could be achieved if the SCOHS process were employed in lieu of an amine unit with a Claus treatment plant.

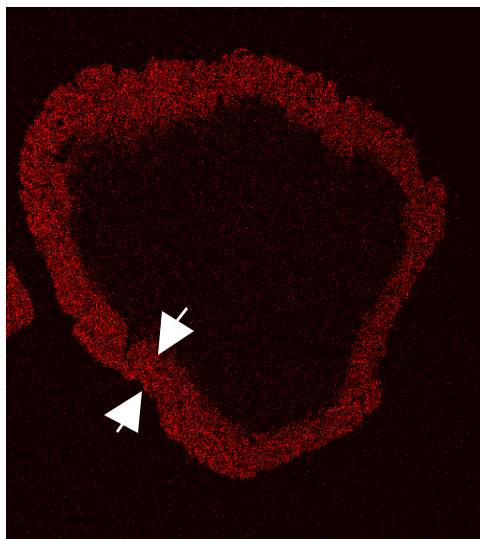


Figure 4. EDS profile of sulfur penetration and retention into the catalyst pellet. The reaction front illustrated is a sharp interface indicating that the intrinsic chemical reaction kinetics are fast relative to intra-particle diffusion.

Table 1. Change in Cost of Electricity with Fixed Bed SCOHS Retrofit (Rutkowski *et al.*, 2001).

	Texaco IGCC		Fixed Bed SCOHS	
	Plant Size 287 MW _e		Plant Size 301 MW _e	
	1000\$/y	\$/kW-y	1000\$/y	\$/kW-y
Capital Charge @ 13.8%	\$57,400	\$200.23	\$56,040	\$186.25
O&M	\$9,718	\$33.90	\$9,026	\$30.00
Sulfur Credit @ \$55/LT	(\$1,046)	(\$3.65)	(\$1,066)	(\$3.54)
Fuel @ \$1.25/ MMBtu	\$22,815	\$79.59	\$23,261	\$77.31
Total	\$88,888	\$310.07	\$87,261	\$288.18
COE @ 80% CF \$/MWh	44.25		41.38	

In summary, the concept of SCOHS was investigated for its ability to remove H₂S to very low levels. With the carbon-based catalyst system utilized in this series of tests, side reactions become more prevalent as temperature is increased and COS evolution becomes more significant as the catalyst sulfur loading is increased. The capillary pressure from the catalyst's micropores may play a role in mitigating this side reaction. Total sulfur levels below 20 ppmv are achievable with the current catalyst at temperatures of 145°C and below. The elemental sulfur that is retained within the catalyst follows a sharp interface progression indicating that the global kinetics was intra-particle diffusion controlled. A highly preliminary economic analysis of the SCOHS process indicates a 7% decrease in the COE (\$/MWh) is possible if this technology is incorporated into IGCC that would otherwise be utilizing cold gas cleanup technology.

Current research is focused on optimization and testing of new catalyst systems that have less of an affinity for CO and on developing engineering design parameters for scale-up and modeling of this novel process.

Literature Cited

- Chen, H. T.; Klett, M. G. and Rutkowski, M. D.; "Sensitivity Effects of Fluidized Bed Hot Gas Desulfurization on IGCC Cost of Electricity." Report prepared by Gilbert/Commonwealth, Inc., Reading, PA. DOE contract No. DE AC01-88FE61660, April (1992).
- Dalai, A. K. and Tollefson, E. L., "Kinetics and Reaction Mechanism of Catalytic Oxidation of Low Concentrations of Hydrogen Sulfide in Natural Gas Over Activated Carbon," The Canadian Journal of Chemical Engineering, Vol. 76, pp. 902-914. October (1998).
- Lagas, J. A., Borsboom, J., and Berben, P. H., "Selective-Oxidation Catalyst Improves Claus Process." Oil & Gas Journal, pp. 68-71. Oct. 10 (1988).
- Kensell, W. and Leppin, D., "Review of the H₂S Direct Oxidation Process." Paper presented at the seventh GRI sulfur recovery conference (1995).
- Meyer, B., Schiffer, H. P., and Walter, H., "Dry Desulfurization of Coal Fuel Gas by Partial Oxidation." Proceedings ICCS '97. Edited by A. Ziegler *et al.* Pp. 1775-1778 (1997).
- Rutkowski, M. D.; Buchanan, T. L.; Klett, M. G. and Schoff R. L.; "Selective Catalytic Oxidation of Hydrogen Sulfide for Simultaneous Coal Gas Desulfurization and Direct Sulfur Production (SCOHS). *Systems Analysis*. Report prepared by Parsons Infrastructure and Technology Group Inc., Reading, PA (2001).